

**AD-A258 345**



## Metallo-Organic Solution Deposition of Ferroelectric PZT Films

Prepared by

R. A. LIPELES and M. S. LEUNG  
Electronics Technology Center  
Technology Operations

and

D. J. COLEMAN  
Mechanics and Materials Technology Center  
Technology Operations

9 September 1992

Prepared for

SPACE AND MISSILE SYSTEMS CENTER  
AIR FORCE MATERIEL COMMAND  
Los Angeles Air Force Base  
P. O. Box 92960  
Los Angeles, CA 90009-2960

Engineering and Technology Group

**DTIC**  
**S** **E** **D**  
ELECTE  
DEC 14 1992

**92-31324**



232

THE AEROSPACE CORPORATION  
El Segundo, California


APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED

**92 12 14 004**

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-88-C-0089 with the Space and Missile Systems Center, P. O. Box 92960, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by B. K. Janousek, Principal Director, Electronics Technology Center. Capt Mark Borden was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

  
\_\_\_\_\_  
QUANG BUI, Lt, USAF  
MOIE Program Manager

  
\_\_\_\_\_  
MARK W. BORDEN, Captain, USAF  
SSUSI/SSULI Project Officer  
DMSP Program Office

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

|   |       |  |   |  |
|---|-------|--|---|--|
| 1a. REPORT SECURITY CLASSIFICATION<br>Unclassified  |       |  | 1b. RESTRICTIVE MARKINGS  |  |
| 2a. SECURITY CLASSIFICATION AUTHORITY   |       |  | 3. DISTRIBUTION/AVAILABILITY OF REPORT<br><br>Approved for public release;<br>distribution unlimited. |  |
| 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE   |       |  |   |  |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)<br>TR-0090(5945-02)-1   |       |  | 5. MONITORING ORGANIZATION REPORT NUMBER(S)<br>SMC-TR-92-42   |  |
| 6a. NAME OF PERFORMING ORGANIZATION<br>The Aerospace Corporation<br>Technology Operations   |       | 6b. OFFICE SYMBOL<br>(if applicable)     | 7a. NAME OF MONITORING ORGANIZATION<br><br>Space and Missile Systems Center                           |  |
| 6c. ADDRESS (City, State, and ZIP Code)<br><br>El Segundo, CA 90245-4691  |       |  | 7b. ADDRESS (City, State, and ZIP Code)<br>Los Angeles Air Force Base<br>Los Angeles, CA 90009-2960   |  |
| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION   |       | 8b. OFFICE SYMBOL<br>(if applicable)     | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>F04701-88-C-0089                                   |  |
| 8c. ADDRESS (City, State, and ZIP Code)   |       |  | 10. SOURCE OF FUNDING NUMBERS   |  |
|   |       |  | PROGRAM<br>ELEMENT NO.  | PROJECT<br>NO.   |
|   |       |  | TASK<br>NO.   | WORK UNIT<br>ACCESSION NO.                                 |
| 11. TITLE (Include Security Classification)<br><br>Metallo-Organic Solution Deposition of Ferroelectric PZT Films   |       |  |   |  |
| 12. PERSONAL AUTHOR(S)<br>Lipeles, Russell A.; Leung, Martin S.; and Coleman, Dianne J.   |       |  |   |  |
| 13a. TYPE OF REPORT   |       | 13b. TIME COVERED<br>FROM _____ TO _____ |   | 14. DATE OF REPORT (Year, Month, Day)<br>1992, September 9 |
| 15. PAGE COUNT<br>22  |       |  |   |  |
| 16. SUPPLEMENTARY NOTATION  |       |  |   |  |
| 17. COSATI CODES  |       |  | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)                     |  |
| FIELD   | GROUP | SUB-GROUP                                | Electro-Optical<br>Film Morphology<br>Hydrolysis<br>MOSD  |  |
|   |       |  | Polymerization<br>PZT<br>Sol-Gel<br>Thermal Treatment   |  |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br><br>The metallo-organic solution deposition [(MOSD) or sol-gel] technique can be used for preparing lead zirconate titanate (PZT) ceramics with a wide range of compositions and crystal structures for electro-optical applications. Film morphology is affected by stoichiometry of the film, hydrolysis and polymerization of the sol-gel solution, and thermal treatment of the deposited material. The lattice parameter decreases with the amount of titanium in PZT in agreement with ceramic data. A slight initial excess of lead in the coating solution is found to improve film morphology. Unlike traditional powder ceramic processing techniques, MOSD permits the growth of small uniform grains that are conducive to achieving consistent electronic and optical properties. Our results show that the properties of films prepared by the MOSD process can be tailored to meet the needs of device applications. |       |  |   |  |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT<br><input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> COME AS RPT. <input type="checkbox"/> DTIC USERS   |       |  | 21. ABSTRACT SECURITY CLASSIFICATION<br>Unclassified  |  |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL   |       |  | 22b. TELEPHONE (Include Area Code)  | 22c. OFFICE SYMBOL   |

## PREFACE

We thank P. M. Adams for x-ray diffraction and G. A. To for FTIR measurements.

|                     |  |
|---------------------|--|
| Accession For       |  |
| NTIS CRA&I          | <input checked="checked" type="checkbox"/> |
| DTIC TAB            | <input type="checkbox"/>                   |
| Unannounced         | <input type="checkbox"/>                   |
| Justification ..... |  |
| By .....            |  |
| Distribution /      |  |
| Availability Codes  |  |
| Dist                | Avail and/or<br>Special                    |
| A-1                 |  |

DTIC QUALITY INSPECTED 3

## CONTENTS

|                                       |    |
|---------------------------------------|----|
| PREFACE .....                         | 1  |
| I. INTRODUCTION .....                 | 5  |
| II. MOSD SOLUTION REACTIONS .....     | 7  |
| III. EXPERIMENTAL .....               | 9  |
| IV. RESULTS AND DISCUSSION .....      | 11 |
| A. Hydrolysis and Crystallinity ..... | 11 |
| B. Composition .....                  | 15 |
| C. Thermal Treatment .....            | 15 |
| V. SUMMARY .....                      | 23 |
| REFERENCES .....                      | 25 |

## FIGURES

|   |    |
|---|----|
| 1. Spectral reflectance FTIR of 800 nm thick PZT films on platinum<br>annealed at 525°C for 30 min .....  | 12 |
| 2. Electron micrographs of PZT films annealed at 525°C .....  | 13 |
| 3. Lattice contraction due to titanium substitution for zirconium in PZT<br>observed by x-ray diffraction in PZT films .....                                      | 16 |
| 4. Surface morphology of PZT films .....  | 17 |
| 5. Light scattering from PZT films deposited on fused silica .....  | 18 |
| 6. Optical micrographs of PZT films .....   | 19 |
| 7. X-ray diffraction $\theta$ -2 $\theta$ scans of PZT films with a 52:48 composition deposited<br>on platinum and consolidated at 300, 400, 500, and 600°C ..... | 21 |

## TABLE

|   |    |
|---|----|
| 1. Effect of Prehydrolysis and Annealing Conditions ..... | 14 |
|---|----|

## I. INTRODUCTION

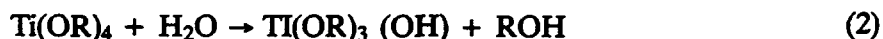
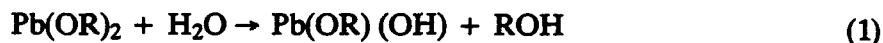
Ferroelectric films are being investigated for use in optical waveguides [1-3], optical switches [3-5], surface acoustic wave transducers [6], and nonvolatile ferroelectric memories [7]. Films for these applications must have reproducible, homogeneous electronic and electro-optical properties. These properties can be obtained in ferroelectric films deposited by metallo-organic solution deposition [(MOSD) or sol-gel] processing. MOSD is a solution-based deposition method where soluble metallo-organic compounds are intimately mixed and polymerized to yield a viscous coating solution. Metallo-organic compounds consist of a central metal atom bonded to organic ligands by oxygen. The solution is used to form a dried, gelatinous film on the substrate by a number of different coating techniques. Ceramic films with a narrow distribution of either microscopic (less than 10 nm) or macroscopic sized grains can be grown from the amorphous film, depending on the thermal processing conditions.

MOSD processing has been applied to a number of different materials, ranging from amorphous glasses to highly crystalline films [8]. In this report, we present the results of our work on the MOSD processing of ceramic lead zirconate titanate (PZT) films. The lanthanum-containing transparent ceramic, lead lanthanum zirconate titanate (PLZT), is an important ferroelectric material for electronic and electro-optical applications. In the PLZT solid solution system, the crystal structure and the electro-optical properties can be tailored for a particular application by changing the stoichiometry [9]. Unlike the lanthanum-free PZT ceramics made from powders, which are translucent or opaque, PZT films are transparent. The challenge in making these PZT films lies in simultaneously obtaining uniform composition, the proper crystal structure, and small grain for low light scattering.

The MOSD processing of films in the PLZT system has been studied extensively. The mixing and reaction of precursors in solution, drying and consolidation, and annealing steps are critical in obtaining dense, optically transparent, ferroelectric films [10-17]. A related solution technique, metallo-organic deposition, uses long-chained carboxylic acid salts to make similar films [18]. In this report, the effects of the solution composition, hydrolysis, and thermal processing on the film morphology, phase segregation, and ease of annealing will be addressed to show the advantages of the MOSD technique.

## II. MOSD SOLUTION REACTIONS

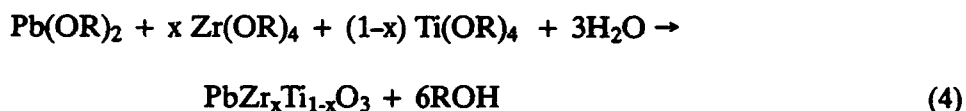
In the MOSD process, metal alkoxides and metal carboxylic acid salts are mixed in solution. These carbon-oxygen-metal bonded metallo-organic compounds are reacted with water to form a metal-oxygen-metal bonded polymer in solution [19]. Polymerization increases the viscosity needed to control the thickness and drying rate of the films. For example, lead alkoxide and titanium alkoxide compounds can be hydrolyzed to form hydroxide-alkoxide compounds:



The alkoxide-hydroxides can react to form the metal-oxygen-metal polymer linkages:



Zirconium alkoxides hydrolyze and react with lead through similar reactions. Further hydrolysis and polymerization can occur, resulting in the polymer precursor for PZT in solution. The complete reaction of the starting materials with water to form  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ , where  $(0 \leq x \leq 1)$ , is:



The amount of water added to the solution is expressed as a molar ratio of water concentration to the total concentration of metals:

$$h = [\text{H}_2\text{O}]/([\text{Pb}] + [\text{Zr}] + [\text{Ti}]) \quad (5)$$

From Eqs. 4 and 5,  $h = 1.5$  corresponds to the stoichiometric amount of water for complete reaction. Polymerization of the precursors increases the viscosity of the solution so that it can be coated on substrates by spinning, dipping, or spraying.

### III. EXPERIMENTAL

$\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  films with compositions specified by  $(x:1 - x)$ , where  $0 \leq x \leq 1$ , were prepared from stoichiometric solutions of metallo-organic precursors [15-17]. Lead 2-ethylhexanoate, zirconium tetrapropoxide, and titanium tetrabutoxide (obtained from Alpha/Ventron) were mixed in isopropanol to form a solution that was about 0.05 M with respect to PZT. After addition of water for hydrolysis and refluxing for about 1 h, the solution was spun on fused silica or platinum substrates. Three-stage thermal processing in air (consisting of drying, consolidation, and annealing steps) was needed to avoid premature crystallization and growth of large, coarse grains. During thermal processing, the film was dried at 100°C to remove the solvent; it was then consolidated at 300°C to remove most of the other organics. The result was the formation of a dense, amorphous film. The coating, drying, and consolidating steps were repeated six to eight times to deposit an amorphous film. The film was then annealed at 525°C to initiate crystallization of small, uniform grains to preserve transparency of the 600-800 nm thick films. Diffuse light scattering was measured at a wavelength of 632.8 nm from samples deposited on fused silica substrates to characterize the optical quality of the films.

## IV. RESULTS AND DISCUSSION

### A. HYDROLYSIS AND CRYSTALLINITY

Reaction of precursors in the solution, the composition of the PZT, and thermal processing conditions are major factors in determining film crystallinity and morphology. Crystalline, perovskite structure is necessary for ferroelectricity in PZT films. First, we showed that partial reaction of precursors in the solution was more effective in producing crystalline PZT than complete reaction of the precursors with water. This observation was made on rhombohedral phase PZT at a ratio of Zr:Ti of 0.55:0.45. The effect of hydrolysis and polymerization of the precursors on crystallization during thermal processing was studied using Fourier transform infra-red (FTIR) spectroscopy. Crystallization of the gel resulted in the emergence of a new vibrational band at  $540\text{ cm}^{-1}$ , assigned to the vibration of metal-oxygen octahedra in the perovskite lattice [20,21]. The intensity in this band was proportional to the amount of crystallization taking place during annealing of the amorphous gel. In Figure 1, the band at  $540\text{ cm}^{-1}$  is larger for  $h = 0$  and  $h = 0.5$  than for the fully reacted sample ( $h = 1.5$ ). The morphology of these films is shown in Figure 2. The porous structure obtained for  $h = 1.5$  indicates that extensive reaction of the precursors formed highly cross-linked and amorphous polymers that were resistant to densification during annealing at  $525^\circ\text{C}$ . At lower water concentrations, the amount of cross linking was reduced. As a result, the oligomers formed were more flexible and more conducive to densification than the highly polymerized solution precursors. Our results indeed showed that complete reaction ( $h = 1.5$ ) resulted in porous films and that less polymerization of the precursors ( $h = 0$  and  $h = 0.5$ ) increased the crystallinity of MOSD films at lower temperature.

The crystallinity of films prepared from solutions with moderate amounts of water ( $h = 0.5$ ) was compared to the crystallinity of films prepared from dry solutions ( $h = 0$ ). Lead titanate (PT) films were cast on platinum substrates from dry ( $h = 0$ ) or partially hydrolyzed ( $h = 0.5$ ) solutions and were consolidated at  $300^\circ\text{C}$ . After deposition of six layers, the films were annealed at either  $550$  or  $600^\circ\text{C}$ . X-ray diffraction was used to measure the intensity of the (110) PZT peak for films listed in Table 1. The peak intensity was proportional to the amount of crystallization in the PZT films. The peak intensities were normalized to the peak intensity of the film annealed at  $600^\circ\text{C}$  for 30 min.

The results in Table 1 indicate that annealing at higher temperatures accelerates crystallization as expected [13]. In addition, these results show that partial reaction ( $h = 0.5$ ) also is responsible for increasing the degree of crystallization compared to samples made from dry ( $h = 0$ ) solutions. In partially hydrolyzed films, the metal-oxygen-metal bonded oligomer acts as a molecular template for subsequent nucleation and crystallite growth. These results show that hydrolysis can be used to decrease the annealing temperature. In certain applications, such as the deposition of ferroelectric films on semiconductor substrates, lowering the processing temperature is beneficial to minimize reactions at the interface.

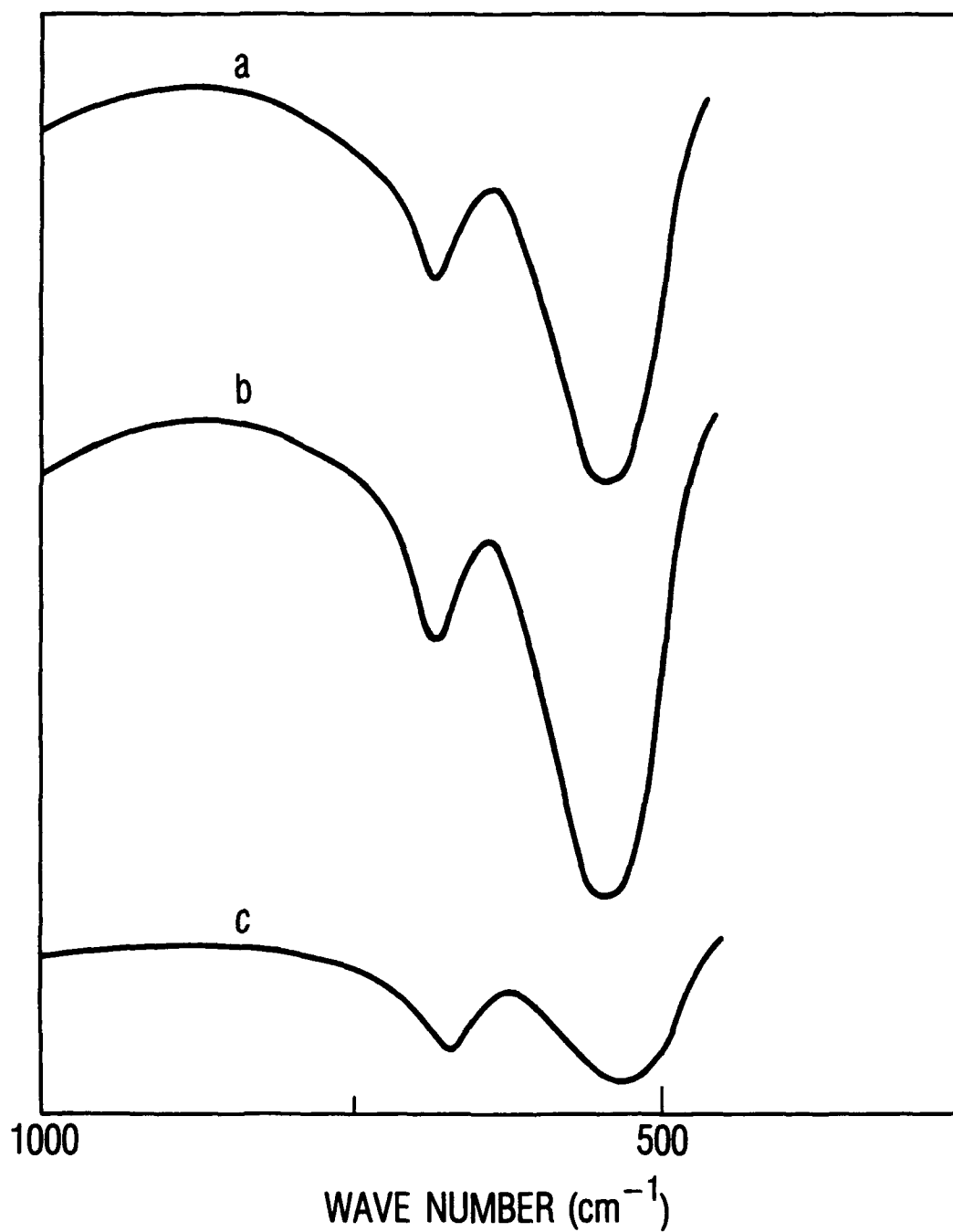
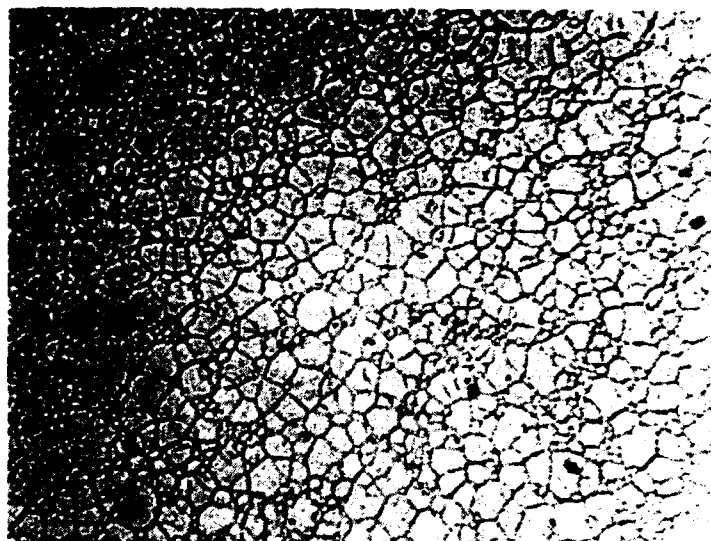
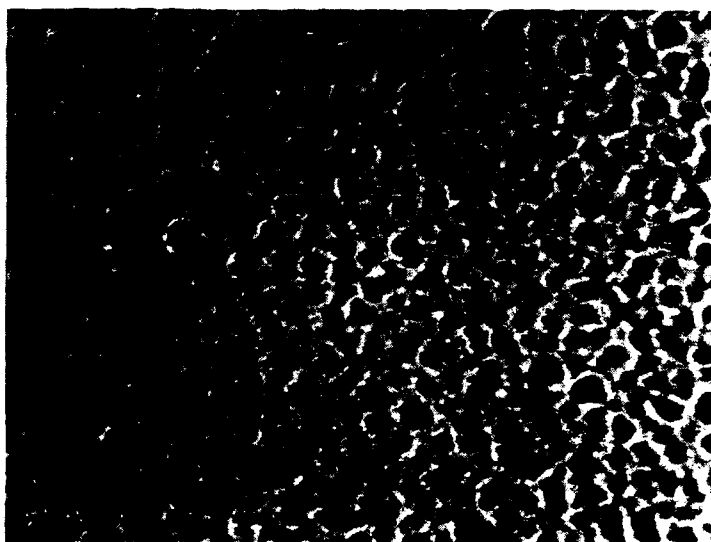


Figure 1. Spectral reflectance FTIR of 800 nm thick PZT films on platinum annealed at 525°C for 30 min with (a)  $h = 0$ , (b)  $h = 0.5$ , and (c)  $h = 1.5$ .



(a)

┌  
└  
10  $\mu\text{m}$



(b)

Figure 2. Electron micrographs of PZT films annealed at 525°C with (a)  $h = 0$  and (b)  $h = 1.5$ .

**Table 1. Effect of Prehydrolysis and Annealing Conditions**

| Hydrolysis,<br>h | Consolidation   |           | Intensity of (110)  |
|------------------|-----------------|-----------|---------------------|
|                  | Temperature, °C | Time, min | Diffraction peak, % |
| 0                | 550             | 30        | 70                  |
| 0                | 550             | 60        | 72                  |
| 0.5              | 550             | 30        | 82                  |
| 0                | 600             | 30        | 79                  |
| 0.5              | 600             | 30        | 100                 |
| 0.5              | 600             | 60        | 99                  |

## B. COMPOSITION

Bulk ceramic structure was obtained in 800 nm thick films prepared by MOSD in the PZT solid solution system. The phases present were determined in films where the zirconium-to-titanium ratio was varied from 60:40 to 0:100. After being annealed at 525°C for 2 h, the crystal structure of the films was characterized by x-ray diffraction. As smaller titanium ions were substituted for zirconium in PZT films, the lattice contracted, as shown from the data in Figure 3. A phase transition from rhombohedral to tetragonal occurred at about 0.52 PbZrO<sub>3</sub> in the film, as expected from the bulk ceramic data reported by Jaffe et al. [22]. This result indicates that the MOSD process can be used to prepare PZT with bulklike properties and that the phase diagram developed from bulk ceramic data can be used to guide the selection of composition and tailor the electronic properties of these thick films.

The micrographs in Figure 4 indicate that film quality depends on the composition of the film. Less cracking was observed in the 20:80 PZT composition (tetragonal structure) compared to the 60:40 composition (rhombohedral structure) films on fused silica substrates. During cooling through the Curie temperature, differences in thermal expansion between the film and the substrate can result in stress and cracking of the film. Lead titanate-rich PZT compositions expand during cooling through the Curie temperature as they change from a cubic to tetragonal structure [23]. Because the substrate contracts during cooling, the film is formed with compressive stress. Lead zirconate-rich films contract when they are cooled through their Curie temperatures [23], resulting in a film held in tension that is subject to cracking. The magnitude of these effects is dependent on the match of the thermal expansion coefficient of the film with that of the substrate. Lower stress and cracking is also correlated to lower diffuse light scattered from titanium-rich films, as shown in Figure 5. In addition to cracking, light is scattered in these films from grain boundaries and surface roughness. On fused silica substrates, high optical quality lead titanate films are easier to grow than compositions containing high lead zirconate concentrations.

We examined the effect of lead concentration in the films during processing. In films that were about 2% deficient in lead, nonuniform nucleation and segregation of a zirconium dioxide phase occurred. In films that were about 2% lead rich, lead oxide acted as a flux that avoided the formation of trace-contaminating oxide phases. Because the excess lead oxide tended to segregate on the edge of the substrate, it did not affect the quality of the films. The morphology of these films is shown in the optical micrographs in Figure 6. The lead-rich films have relatively few features, while the lead-poor films have large, coarse grains.

## C. THERMAL TREATMENT

The perovskite crystal structure, easily obtained at high temperatures, is necessary for ferroelectricity in PZT films. However, in many applications, consolidation and crystallization must be achieved at the lowest possible temperatures. Low temperature processing minimizes microcracking by stress that results from differential thermal expansion of the substrate and

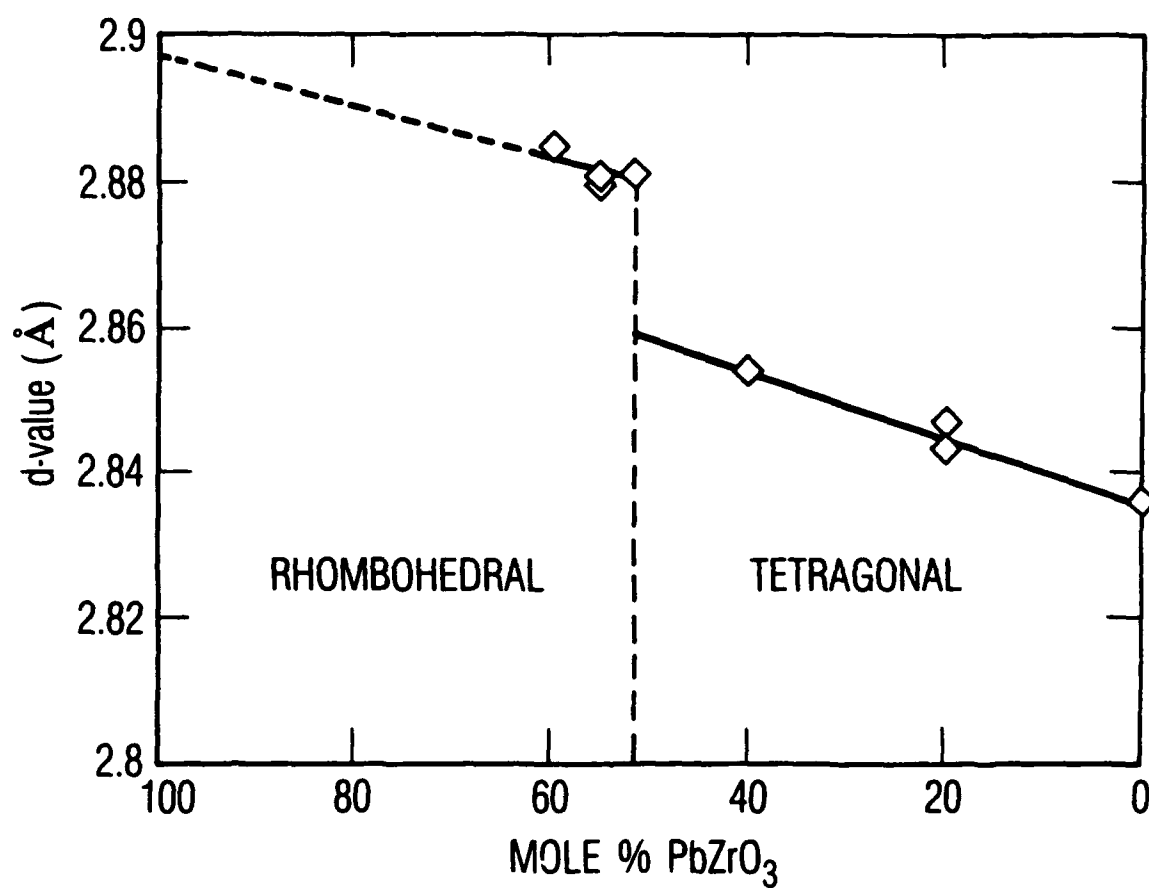


Figure 3. Lattice contraction due to titanium substitution for zirconium in PZT observed by x-ray diffraction in PZT films. Two regions were observed consistent with the ceramic: a high-zirconia rhombohedral phase and a high-titanate tetragonal phase.



(a)

20  $\mu\text{m}$



(b)

Figure 4. Surface morphology of PZT films with (a) high zirconium concentration, 60:40, and (b) high titanium, 20:80. Note the presence of stress-induced microcracking and large cracks in (a), which is minimized in (b).

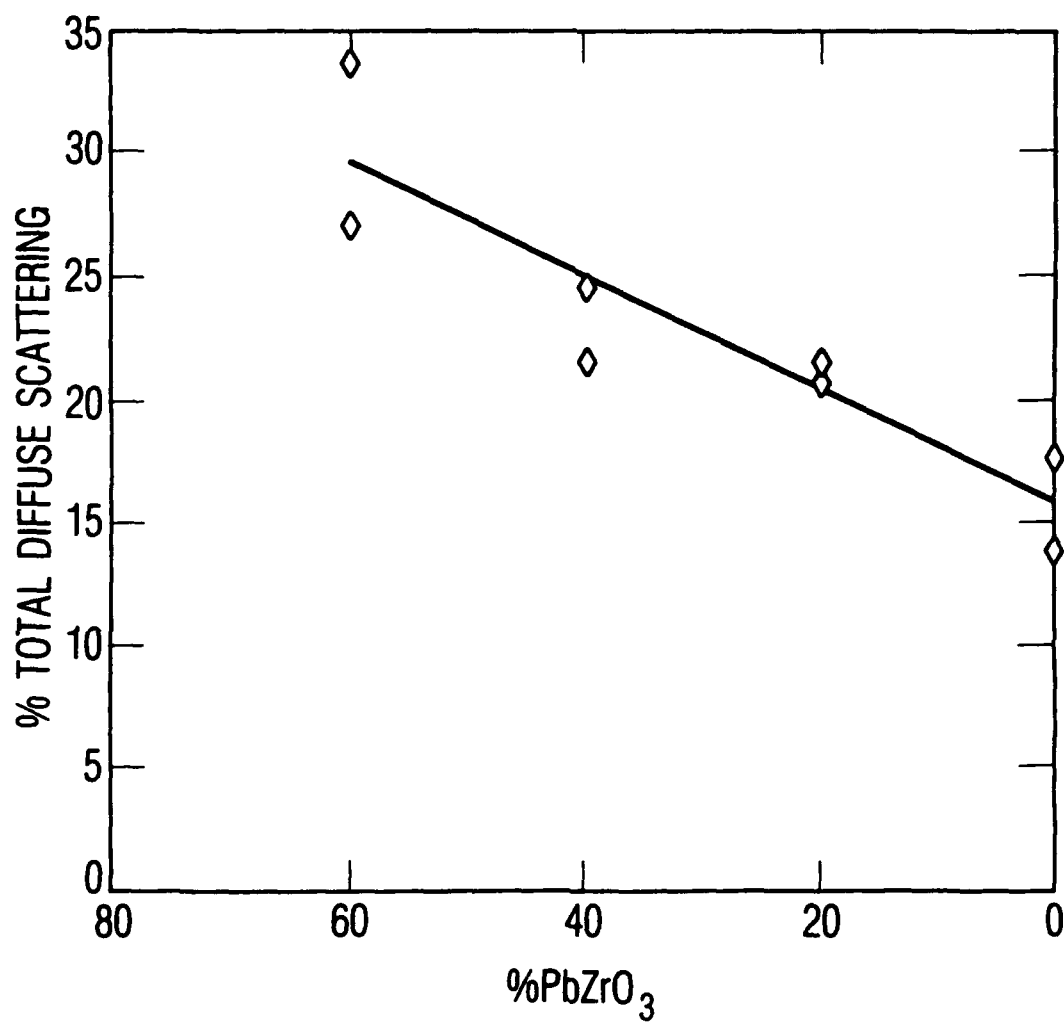
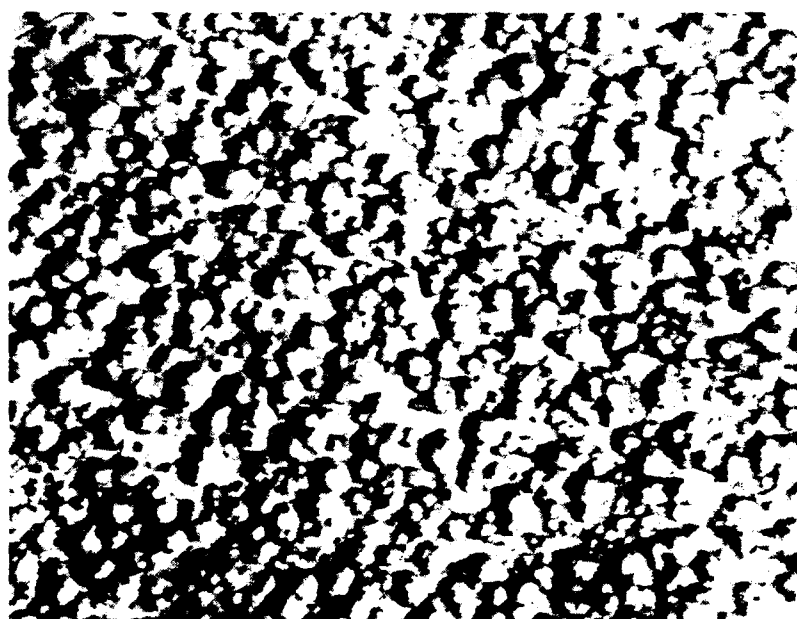


Figure 5. Light scattering from PZT films deposited on fused silica.



(a)

┌┐  
10  $\mu\text{m}$



(b)

Figure 6. Optical micrographs of PZT films processed with (a) excess lead oxide or (b) low lead oxide.

film. In addition, thermal diffusion and contamination of the film or substrate are reduced. Consolidation at low temperatures is particularly desirable to avoid reactions of the hot organic by-products with the substrate. In Figure 7, we show the effect of consolidation temperature on the crystallinity of films annealed at 550°C. In films consolidated at 500°C, the growth of the perovskite structure was reduced by the presence of a cubic pyrochlore-like phase related to  $\text{Pb}_2\text{Ti}_2\text{O}_6$  [24]. The films consolidated at 300 and 400°C are perovskite [25], with a trace amount of the pyrochlore phase. The presence of the trace pyrochlore phase is further reduced at 600°C. These results and the time-temperature-transformation diagrams published by Chen et al. [14] indicate that PZT films can be consolidated (and annealed) at a wide range of temperatures. Selection of processing temperatures will depend on the reactivity and thermal expansion coefficients of the substrate and PZT film.

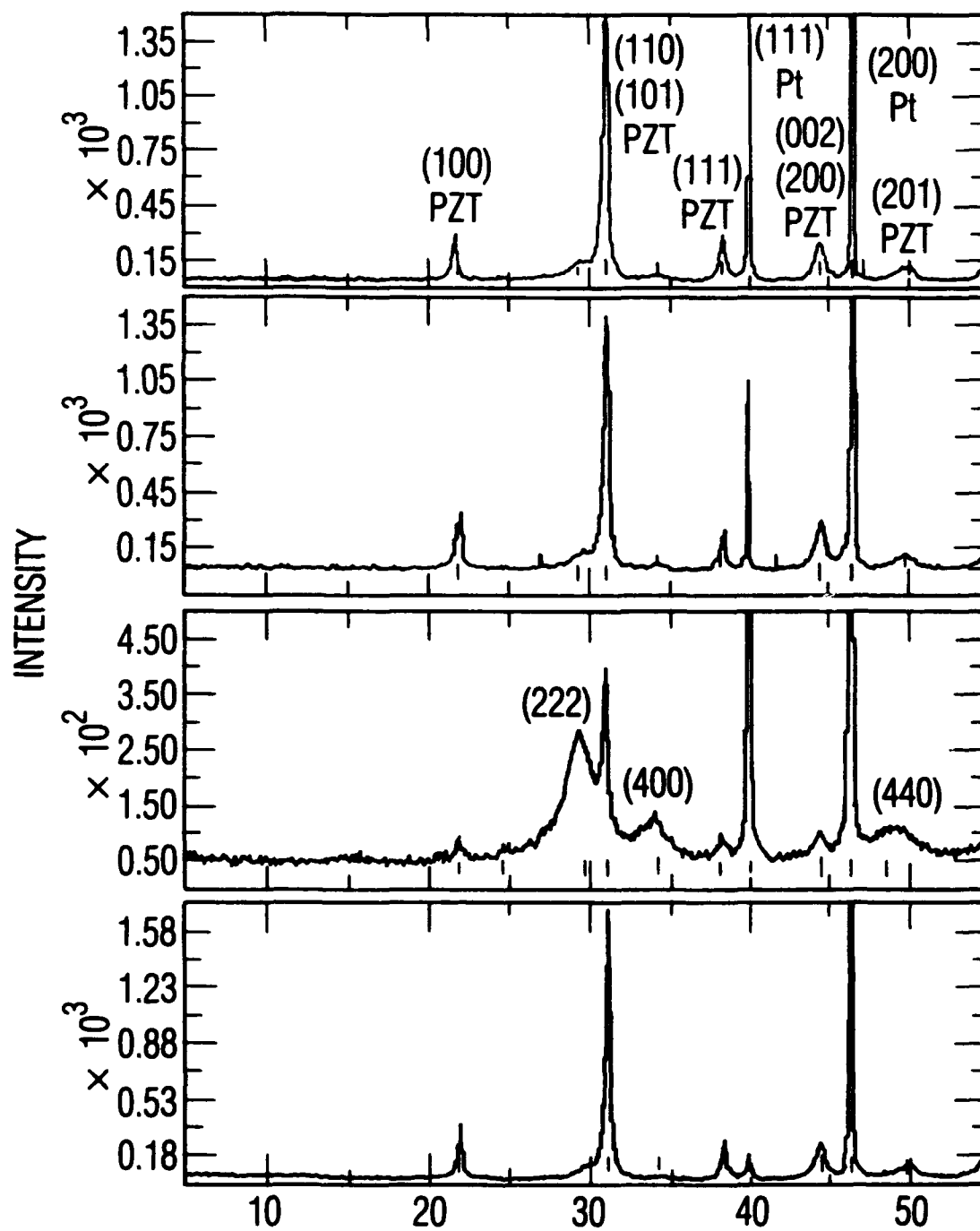


Figure 7. X-ray diffraction  $\theta$ - $2\theta$  scans of PZT films with a 52:48 composition deposited on platinum and consolidated at (from the top) 300, 400, 500, and 600°C.

## V. SUMMARY

In summary, the MOSD technique can be used for making a wide range of PZT compositions with bulk structure and properties. Film morphology is affected by metal stoichiometry, hydrolysis and polymerization of the sol-gel solution, and thermal treatment. The PZT lattice parameter decreases with the amount of titanium in PZT, in agreement with ceramic data. A slight initial excess of lead in the coating solution improves film morphology. Unlike traditional powder ceramic techniques, MOSD permits the growth of small uniform grains. Films can be consolidated prior to crystallization at temperatures from 275 to 600°C, except for about 500°C, where the pyrochlore is stable. The ability to tailor these properties by the MOSD process will result in electro-optical films for new device applications.

## REFERENCES

1. T. Kawaguchi, H. Adachi, K. Setsune, O. Yamazaki, and K. Wasa, "PLZT Thin-Film Waveguides," Appl. Opt., vol. 23, pp.2187-2191, 1984.
2. H. Higashino, T. Kawaguchi, H. Adachi, T. Makino, and O. Yamazaki, "High Speed Optical TIR Switches Using PLZT Thin-Film Waveguides on Sapphire," Japan. J. Appl. Phys., vol. 24, Suppl. 24-2, pp. 284-286, 1989.
3. M. Ishida, H. Matsunami, and T. Tanaka, "Electro-optic Effects of PLZT Thin Films," Appl Phys. Lett., vol. 31, pp. 433-434, 1977.
4. C. E. Land, "Longitudinal Electro-optic Effects in Polycrystalline PLZT Thin Films," Proceedings of the American Ceram. Soc., Cincinnati, OH, May 1988.
5. S. J. Martin, M. A. Butler, and C. E. Land, "Ferroelectric Optical Image Comparator Using PLZT Thin Films," Electron. Lett., vol. 24, pp. 1486-1487, 1988.
6. S. B. Krupanidhi, M. Sayer, K. El-Assal, C. K. Jen, and G.W. Farnell, "Fabrication and Characterization of Piezoelectric Films for SAW and Acoustic Microscopy," J. Canadian Ceram. Soc., vol. 53, pp. 28-33, 1984.
7. J. F. Scott and C. A. Paz de Araujo, "Ferroelectric Memories," Science, vol. 246, pp. 1400-1405, 1989.
8. J. D. Mackenzie, "Applications of the Sol-gel Method: Some Aspects of Initial Processing," in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, Eds., John Wiley & Sons, New York, 1986, pp. 113-122.
9. G. H. Haertling and C. E. Land, "Hot-Pressed (Pb,Lu) (Zr,Ti) O<sub>3</sub> Ferroelectric Ceramics for Electrooptic Applications," J. Am. Ceram. Soc., vol. 54, pp. 1-11, 1970.
10. J. Fukushima, K. Kodaira, and T. Matsushita, "Preparation of Ferroelectric PZT Films by Thermal Decomposition of Organometallic Compounds," J. Mat. Sci., vol. 19, pp. 595-598, 1984.
11. K. D. Budd, S. K. Dey, and D. A. Payne, "The Effect of Hydrolysis Conditions on the Characteristics of PbTiO<sub>3</sub> Gels and Thin Films," Mat. Res. Soc. Symp. Proc., vol. 73, pp. 711-716, 1986.
12. K. D. Budd, "Structure Evolution in Sol-gel Derived Lead Titanate-Based Materials, and Application to the Processing of Thin Dielectric Layers," PhD Thesis, University of Illinois at Urbana-Champaign, 1986.
13. K. D. Budd, S. Y. Dey, and D. A. Payne, "Sol-Gel Processing of PbTiO<sub>3</sub>, PbZrO<sub>3</sub>, PZT, and PLZT Thin Films," Brit. Ceram. Soc. Proc., vol. 36, pp. 107-121, 1985.

14. K. C. Chen, A. Janah, and J. D. Mackenzie, "Crystallization of Oxide Films Derived From Metallo-organic Precursors," Mat. Res. Soc. Symp. Proc., vol. 73, pp. 731-736, 1986.
15. R. A. Lipeles, N. A. Ives, and M. S. Leung, "Sol-gel Processing of Lead Zirconate Titanate Films," Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, Eds., John Wiley & Sons, New York, 1986, pp. 320-326.
16. R. A. Lipeles, D. J. Coleman, and M. S. Leung, "Effects of Hydrolysis on Metallo-organic Solution Deposition of PZT Films," Mat. Res. Soc. Proc., vol. 73, Better Ceramics Through Chemistry, C. J. Brinker, D. E. Clark, and D. L. Ulrich, Eds., Materials Research Society, Pittsburgh, PA, 1986, pp. 665-670.
17. R. A. Lipeles and D. J. Coleman, "Effect of Drying and Annealing on Metallo-organic Solution Deposition of PZT Films," in Ultrastructure Processing of Advanced Ceramics, J. D. Mackenzie and D. R. Ulrich, Eds., Wiley-Interscience, New York, 1988, pp. 919-924.
18. R. W. Vest and J. Xu, "PbTiO<sub>3</sub> Films from Metallo-organic Precursors," IEEE Trans. Ultrason. Ferroelectr. and Freq. Control, vol. 35, pp. 711-717, 1988.
19. D. C. Bradley, R. C. Mehrotra, and D. P. Gaur, Metal Alkoxides, Academic Press, New York, 1978, pp. 150-167.
20. J. T. Last, "Infrared-absorption Studies on Barium Titanate and Related Materials," Phys. Rev., vol. 105, pp. 1740-50, 1957.
21. W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, "Far-infrared Dielectric Dispersion in BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and TiO<sub>2</sub>," Phys. Rev., vol. 126, pp. 1710-21, 1962.
22. B. Jaffe, W. Cook, and H. Jaffe, Piezoelectric Ceramics, Academic Press, London, 1973, p. 135.
23. G. Shirane, K. Suzuki, and A. Takeda, "Phase Transitions in Solid Solutions of Lead Zirconate and Lead Titanate: II. X-ray Study," J. Phys. Soc. Japan, vol. 7, pp. 12-18, 1952.
24. Joint Committee on Powder Diffraction Standards, Powder Diffraction File, Pb<sub>2</sub>Ti<sub>2</sub>O<sub>8</sub>, International Center for Diffraction Data, Swarthmore, PA, 1976, card no. 26-142.
25. Joint Committee on Powder Diffraction Standards, Powder Diffraction File, PbZr<sub>0.52</sub>Ti<sub>0.48</sub>O<sub>3</sub>, International Center for Diffraction Data, Swarthmore, PA, 1983, card no. 33-784.

## TECHNOLOGY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Technology Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual Technology Centers:

**Electronics Technology Center:** Microelectronics, solid-state device physics, VLSI reliability, compound semiconductors, radiation hardening, data storage technologies, infrared detector devices and testing; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; cw and pulsed chemical laser development, optical resonators, beam control, atmospheric propagation, and laser effects and countermeasures; atomic frequency standards, applied laser spectroscopy, laser chemistry, laser optoelectronics, phase conjugation and coherent imaging, solar cell physics, battery electrochemistry, battery testing and evaluation.

**Mechanics and Materials Technology Center:** Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; development and analysis of thin films and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; development and evaluation of hardened components; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion; spacecraft structural mechanics, spacecraft survivability and vulnerability assessment; contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; lubrication and surface phenomena.

**Space and Environment Technology Center:** Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation; propellant chemistry, chemical dynamics, environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.